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Ferroelectric Polarization Switching in Nylon 11

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Synopsis

Cold drawn nylon 11 films, which were prepared by stretching the melt quenched films to a draw ratio of 2.8:1 at room temperature, were found to exhibit an electric displacement vs electric field hysteresis loop. The results confirmed that the nylon 11 film exhibited ferroelectric behavior at room temperature or lower. The coercive fields were 65, 98, 125, 160 and 215 MV/m at 20, 0, -20, -40 and -60°C and the remanent polarization at -20°C (where there was considerably less dc conduction) was 56 mC/m². Switching of the polarization was almost completed within 20 ms.

INTRODUCTION

Ferroelectric behavior in polymeric materials has been demonstrated in very few polymers (poly(vinylidene fluoride) [PVF₂]¹ and its copolymers²) at present. Other than these, nylon 11 has been reported to exhibit relatively large piezoelectric and pyroelectric activities.³⁻⁶ Recently, Mathur et al.⁷ studied uniaxially stretched nylon 11 films initially melt quenched or slowly cooled and plasticized. They found that uniaxially stretched nylon 11 quenched films exhibit much higher piezoelectric activity than that observed for unoriented films under identical poling conditions (50 MV/m at 75°C). They also demonstrated that the polarity of the piezoelectric constants reversed and exhibited hysteresis-like behavior if the samples were subjected to a series of static positive and negative poling fields.

A few researchers^{6,8} have referred to the D vs E hysteresis characteristics of nylon 11, where D is the electric displacement and E the electric field. However, their conclusion was that the D vs E hysteresis studies revealed no hysteresis in any of the samples tested.

Recent investigations of nylon 11 films raised fundamental but important questions about whether or not nylon 11 is a ferroelectric material. The results of Mathur et al.⁷ may provide an answer to the question. The previous D vs E hysteresis measurements of other researchers, however, appear to provide a negative answer.

It is well known that typical ferroelectric polymers such as PVF₂^{1,9} and P(VF₂/TrFE)^{2,10} exhibit clear D vs E hysteresis loops

and the polarization reversal is almost complete within several milliseconds, even when the temperature is a few tens of degrees below the glass transition point.^{11,12} These phenomena have been considered to be the direct result of a ferroelectric dipolar reorientation within the polar crystals.¹³

In order to answer the question as to whether or not nylon 11 is a ferroelectric material, it is essential to observe similar D vs E hysteresis characteristics and polarization switching transients in nylon 11 to compare the observed behavior to that of PVF₂. We, therefore, began to study the D vs E hysteresis characteristics in nylon 11 by examining several parameters. Many samples were prepared under different conditions. Finally, we observed very clear D vs E hysteresis characteristics in nylon 11. Comprehensive results will be demonstrated later. In the present paper, we demonstrate typical results of the D vs E hysteresis characteristics of nylon 11 and also show how fast the polarization reversal takes place.

EXPERIMENTAL

The nylon 11 films used in the present study were initially prepared by melt pressing nylon 11 pellets supplied by Rilsan Co. (Glen Rock, NJ). The molten film (205 - 210°C) sandwiched by aluminum foils was quenched by immersing it into water at room temperature (23 - 25°C). The quenched film was then uniaxially oriented by stretching it to a draw ratio of 2.8:1 at room temperature. The final film thickness of the sample was 10 - 14 μm . Silver paint electrodes, each about 10 mm² in area, were coated

on opposing surfaces of the film. Note that the sample after quenching was never heated above room temperature.

The D vs E hysteresis characteristics were measured at several temperatures by using a high voltage power supply and a picoammeter (Keithley 485) connected in series with the sample. The period of the triangular high voltage wave form was 640 s.

The time domain characteristics of polarization switching were measured at 20°C using a high voltage power supply equipped with an SCR switch and a digital waveform recorder (Sonny-Tektro-nix 390 AD). The switching time of the SCR switch is about 1 μ s.

Operation of various functions in the system was consigned to a microcomputer (IBM-XT) which also performed the task of data processing.

RESULTS

D - E Hysteresis Characteristics

Figure 1 (a) shows the current density vs electric field (J vs E) characteristics at temperatures from T=20 to -60°C when the sample is subjected to a triangular shaped electric field with maximum field, E_p , of 160 (for T=20°C) or 250 MV/m (for T=0 to -60°C). Figure 1 (b) shows the J vs E characteristics of one of the typical ferroelectric polymers, PVF₂, at temperatures from 20 to -140°C for comparison. The maximum fields were set similar to those of the nylon 11 measurements (E_p =160 MV/m for T=20°C and 250 MV/m for others). The peak height of the curve at T=20°C is relatively small because while the period of the field is kept constant, the value of E_p is smaller. When the temperature is 0°C

or higher, the J vs E curves of nylon 11 show a certain amount of dc conduction while the PVF_2 sample does not. The conduction component usually consists of an ohmic (linear) component and a nonlinear component. The nonlinear component normally obeys an exponential dependence on E and has a strong temperature dependence. The J vs E curves at $T = -20$ to -60°C on the ramp down cycle are apparently similar to the dc conduction curve. These characteristics, however, can be distinguished from the former because of their lower temperature dependence. This characteristic reflects the fact that a certain number of dipoles still continue to reorient even at the maximum electric field. Figure 1 (c) shows the corrected J vs E characteristics of nylon 11 obtained by subtracting the dc conduction current and the current due to the uncompleted dipolar reorientation.

It is evident that nylon 11 exhibits a sharp current peak which indicates a polarization reversal phenomenon. The peak positions or the coercive fields, E_c , are 65, 98, 125, 160 and 215 MV/m for 20, 0, -20, -40 and -60°C , respectively. These curves are essentially the same as those of PVF_2 , especially when the PVF_2 sample is at -60°C or lower. The temperature dependence of E_c for nylon 11, however, is much larger than that of PVF_2 .

The D vs E characteristics obtained by integrating J of each curve in Figure 1 (c) with respect to time are shown in Figure 2. From the sharp peak obtained in each of the J vs E curves in Figure 1 (c), it is apparent that nylon 11 exhibits the typical D vs E hysteresis loops found in ferroelectric materials. The values of remanent polarization determined by the intercept of

each loop with the D-axis are 68, 64, 56, 46 and 31 mC/m² for T=20, 0, -20, -40 and -60°C, respectively.

Polarization Switching Transients

The time dependence of the switching current densities, J_f and J_r , measured at 20°C under pulsed electric fields of 100, 120 and 140 MV/m are shown in Figure 3, where J_f and J_r represent current densities obtained when the electric field is applied in the forward and reverse directions, respectively. These data are almost steady characteristics after the tenth switching cycle. The magnitude of J_r rapidly increases, compared to that of J_f , as the pulsed field reaches 100 MV/m or more. As we can see from the $\log J_r$ vs $\log t$ plot in the figure, the curve obeys a power law in the short time region and then exhibits a shoulder. These features are very similar to those observed for PVF₂ at $T \approx -70^\circ\text{C}$.¹²

Figure 4 shows the time dependence of the charge densities D_f (forward) and D_r (reverse) measured under the same conditions as those in Figure 3. The build-up of the polarization reversal charge is clearly seen on these curves. The polarization reversal is almost complete in a few tens of milliseconds under 140 MV/m at 20°C.

DISCUSSION

Cold drawn nylon 11 films show D - E hysteresis characteristics and polarization switching transients clearly. Except for PVF₂ and its copolymers, no other polymeric materials have been reported to exhibit these clear ferroelectric characteristics.

The stable and rectangular type D vs E hysteresis loops and fast polarization reversal phenomena distinguish ferroelectric behavior from the conduction behavior of mobile ions and confirms the phenomenon to be dipolar in origin. This implies that the cold drawn nylon 11 is a ferroelectric material at or below room temperature.

The origin of observed ferroelectric behavior, from a crystallographic point of view, is characteristic of a crystal lattice whose unit cell is noncentrosymmetric and polar. Insufficient information is available about the crystal structure of cold drawn nylon 11 at present. However, from the cell parameters reported by Little¹⁴ and the value of the dipole moment of the amide group (about 3.7 Debye³), we can estimate that the spontaneous polarization of a nylon 11 crystal is 68 mC/m². The measured bulk remanent polarization may be estimated as $P_r = f L P_s$,¹⁵ where f is the portion of reorientable dipoles and L is given as $3\epsilon / (2\epsilon + \epsilon_c)$, which is applicable to a two phase model consisting of spherical crystals with dielectric constant ϵ_c , distributed in an amorphous matrix with dielectric constant ϵ . If we use this relationship, we can estimate the maximum P_r to be 68 mC/m² at low temperatures, where $\epsilon \approx \epsilon_c$ or 102 mC/m² at high temperatures, where ϵ becomes almost infinite due to the dc conduction. If we use the measured values of P_r , 68 — 46 mC/m² at $T = 20 - -40^\circ\text{C}$, we can estimate, approximately, that 60 to 80 % of the dipoles are reoriented by the external electric field.

We have shown that nylon 11 exhibits essentially the same ferroelectric characteristics as those of PVF₂. It seems, however, also important to note that nylon 11 has a different molecu-

lar chain arrangement from that of PVF₂ and exhibits some different characteristics from those of PVF₂: The arrangement of molecular chains in nylon 11 has been considered to result from close-packing of paraffinic chains and N-H...O hydrogen bonds.³ The long, nonpolar, [CH₂]₁₀ unit and the hydrogen bond distinguish nylon 11 from PVF₂. These arrangements are based on observations from nylon 11 samples prepared by a slow cooling procedure or a high temperature annealing procedure. We did not find any D vs E hysteresis characteristics in such samples and the results were similar to these obtained by previous researchers. Only the cold drawn samples showed typical ferroelectric behavior. This result suggests that the somewhat distorted structure of the paraffinic chains and hydrogen bonds resulting from the quench and cold-draw process may play an important role in allowing for field-induced rotation of the amide-group dipoles. Similar behavior is exhibited by PVF₂, i. e. quenched cold-drawn samples exhibit enhanced dipole switching.

CONCLUSION

Cold drawn nylon 11 exhibits ferroelectric behavior at or below room temperature based on our observations of typical D vs E hysteresis characteristics and polarization switching transients. The coercive fields were 65, 98, 125, 160 and 215 MV/m at 20, 0, -20, -40 and -60°C and the remanent polarization at -20°C (where there was considerably less dc conduction) was 56 mC/m². Switching of the polarization was almost completed within 20 ms.

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Figure captions

Figure 1 1 (a) Current density vs electric field (J vs E) characteristics of cold drawn nylon 11 film when the sample is subjected to triangular shaped electric field. 1 (b) The J vs E characteristics of PVF_2 . 1 (c) The corrected J vs E characteristics of the nylon 11 film obtained by subtracting the dc conduction current and the current due to the uncompleted dipolar reorientation.

Figure 2 The D vs E characteristics obtained by integrating J from each curve in Figure 1 (c) with respect to time.

Figure 3 The time dependence of the switching current densities, J_f and J_r , where J_f and J_r represent current densities under a pulsed electric field applied in the forward and reverse directions, respectively.

Figure 4 The time dependence of the charge densities D_f (forward) and D_r (reverse) measured under the same conditions as those in Figure 3.

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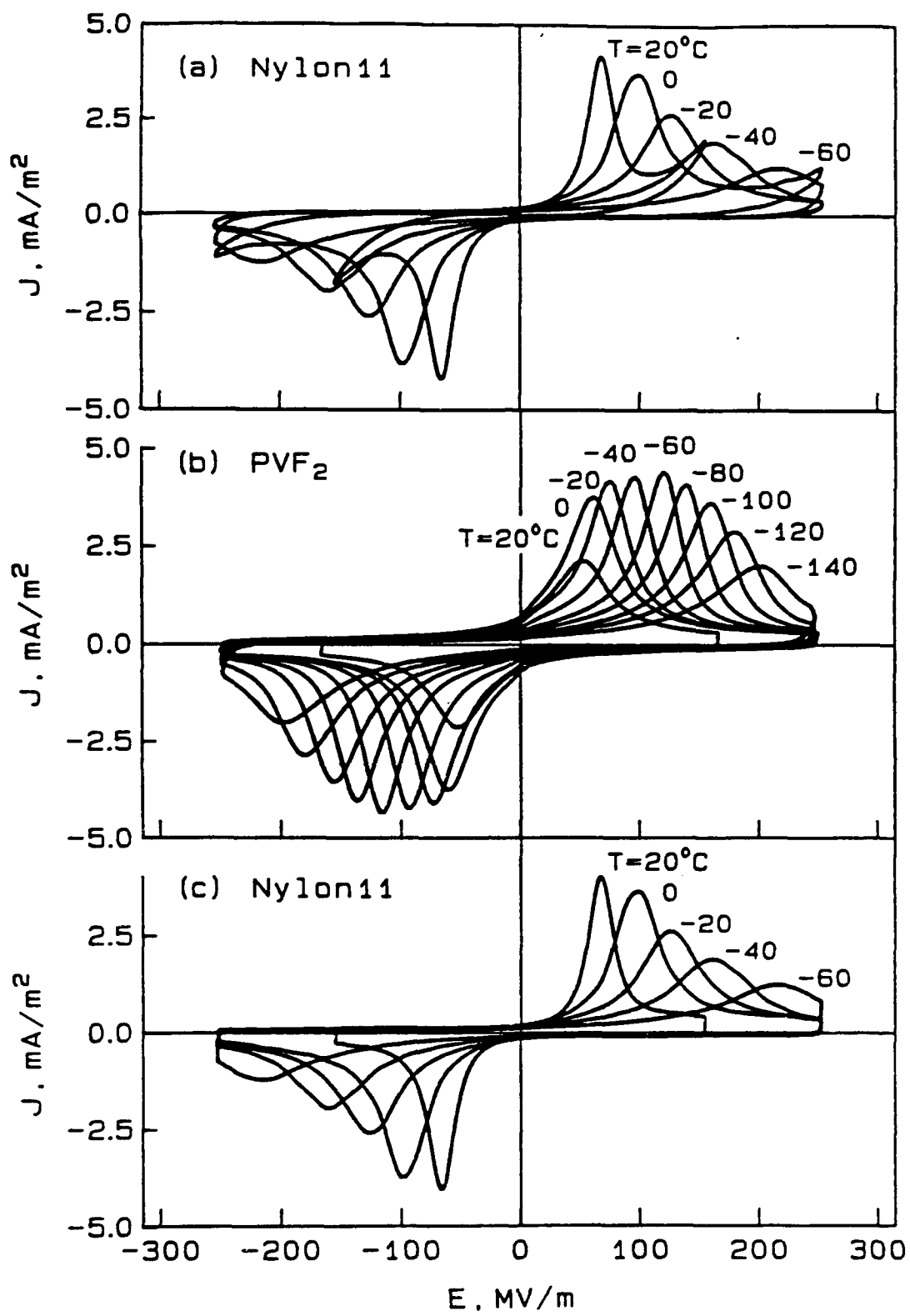


Figure 1

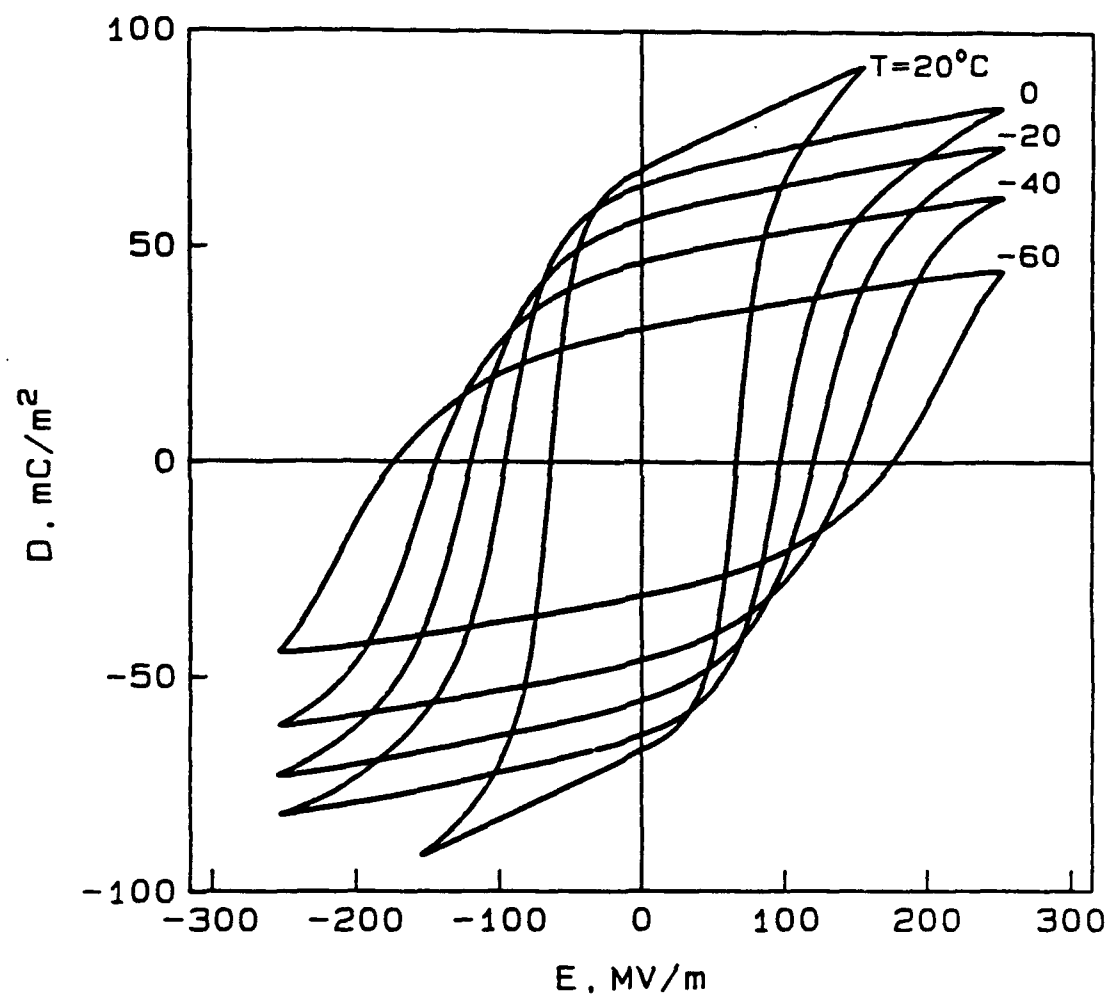


Figure 2

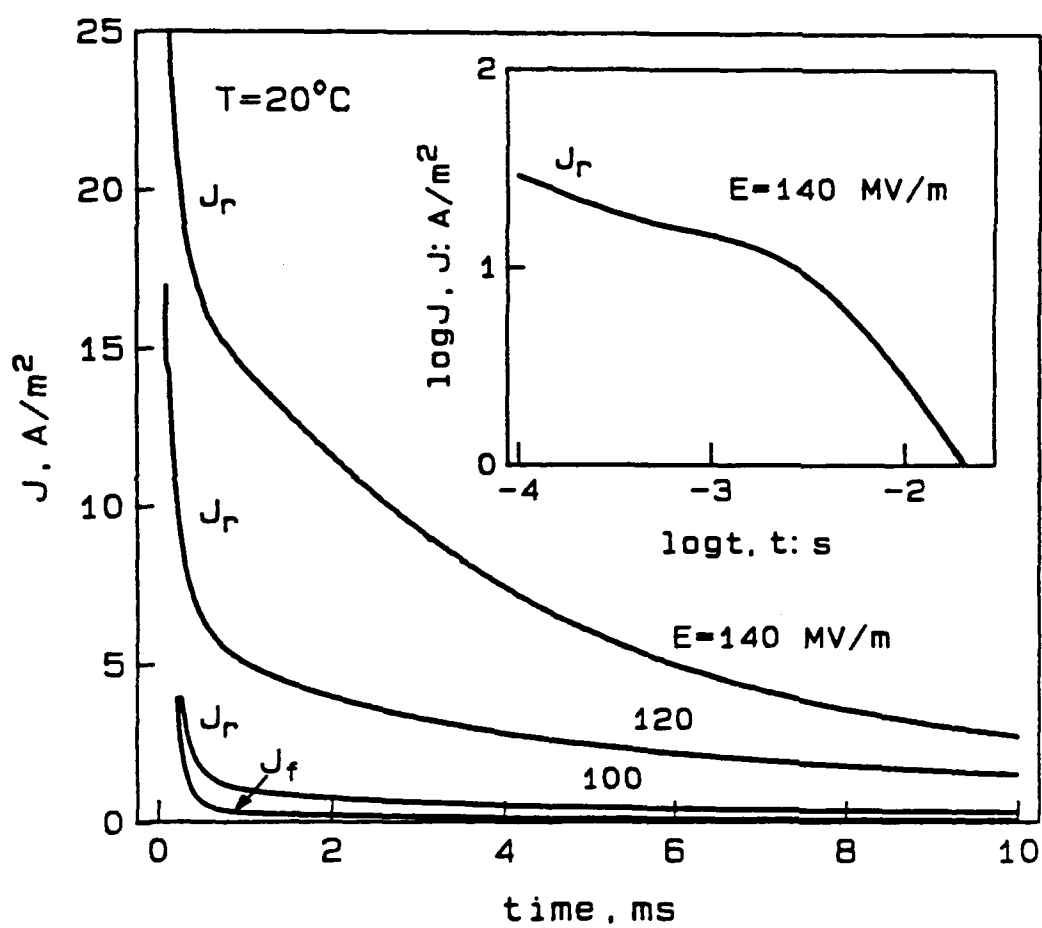


Figure 3